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(54) PROCEDURE AND DEVICE FOR AUTOMATIC SAMPLING WITH A FLAMELESS ATOMIC ABSORPTION SPECTROMETER

(71) We, BODENSEEWERK PERKIN-ELMER & Co. GmbH, of Uberlingen/See West Germany, a Body Corporate organised and existing under the laws of West Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

With flameless atomic absorption spectrometry, where the atomic cloud whose absorption is measured, is generated in a graphite tube of a heated graphite atomizer, the sample to be analysed is in general introduced through a wall aperture into the graphite tube. Only very small quantities of the order of up to about 20 microlitres are normally introduced by means of a micropipette into the graphite tube. This procedure is disadvantageous when carrying out series of atomic absorption measurements, as a disproportionately large amount of time and the continuous presence of an operator is required.

According to the invention, the samples to be analysed are introduced through an aperture in the graphite tube by means of sample containers which are open at both ends and are arranged in sequence on a sample holding device, each sample container in succession being moved to a position, from which the sample is introduced into the graphite tube, and then returned to the initial position in the sample holding device after which the next sample container is similarly treated. With this procedure, the sample containers can be filled independently in advance of the time of analysis and be fitted into the sample holding device. The specific advantage of this procedure consists in the fact that when carrying out the measuring series, the sample containers can be inserted one after the other into the insertion aperture of the graphite tube, so that the samples can be introduced by a particularly simple method.

Preferably each container is moved into position above the insertion aperture of the graphite tube, is pressed into the insertion aperture against the force of a spring by means of an introduction device, and is held in this position until transfer of the sample into the graphite tube has been completed. The use of spring control ensures that the sample container always follows the individual movements of the introduction device, vertical movement of the latter being particularly convenient.

The use of capillary containers has the advantage of retaining the sample liquid by capillary action, but requires the use of pressure for transferring the sample from the sample container into the graphite tube. Inert gas from the same source as the inert gas flow required for operation of the heated graphite atomizer can advantageously be used for this purpose. The same gas source can also be used to produce the movement of each successive container into position in the insertion aperture of the graphite tube.

Apparatus according to the invention for carrying out the above method comprises a sample holding device located above the graphite tube cell and capable of stepwise movement for bringing successive sample containers in the form of micro-pipette tips open at both ends into a sampling position in line with the insertion aperture of the graphite tube, an introduction device in the form of a slider which is movable up and down in a guide for inserting the sample container in the sampling position in the insertion aperture, a source of pressure gas for forcing out the sample from the container into the graphite tube in the lowered position of the slider and a control device for synchronizing the actuation of the introduction device, the movement of the sample holding device and release of gas from the pressure source.

It is preferable to provide a common support for the sample holding device and for the introduction device and for the heated

graphite atomizer to be removably attached to this support. The relationship between the individual items is thus determined and the components are maintained in their correct positions in relation to each other.

The sample holding device is preferably formed as a turntable, provided near its edge with holders for micro-pipette tips, each holder conveniently being slidable vertically in a guide under spring control. When each micro-pipette is moved into the insertion aperture of the graphite tube by means of the slider, it needs to be held against the spring force.

The invention will now be described in more detail, by way of example, with reference to the accompanying drawings, in which:—

Figure 1 is a sectional elevation of apparatus according to the invention in its inoperative position:

Figure 2 is a corresponding view showing the apparatus in its operative position, where a micropipette tip is inserted into the insertion aperture of a graphite tube;

Figure 3 is a plan view; and

Figure 4 is a fragmentary view, partially diagrammatic and showing an alternative form of control means.

As illustrated in Figures 1 to 3, the apparatus includes a support member 10, a heated graphite atomizer 12 detachably mounted thereon, and an introduction device indicated generally at 14 mounted on the support member 10 above the atomizer 12. A sample holding device in the form of a turntable 16 is mounted on a shaft 18 for stepwise rotation by a drive, not shown. The shaft 18 is carried by the support member 10 at 20, whereby the support member 10 determines the relative positional relationships of the turntable, the heated graphite atomizer and the introduction device, with respect to each other. The turntable 16 carries a ring of sample holding members 22, which are arranged for vertical movement with respect thereto. A spring 24 serves to urge each holding member towards its upper position. Each holding member has an arm portion 26 extending outwardly of the periphery of the turntable and an aperture 28 is provided therein for receiving a sample container. The sample containers are in the form of micro-pipette tips 30 that are open at both ends, the sample 32 being contained therein by means of capillary action. Accordingly, a large number of sample containers 30 can be inserted in the holding members 22 of the turntable and kept therein without the sample liquid being lost.

The heated graphite atomizer 12 contains a graphite tube 34 of a graphite tube cell having an insertion or introduction aperture 36, which is so positioned that, when a sample holder holding a micro-pipette tip 30 is in its sampling position, it is in alignment with the introduction aperture 36. A stream of inert gas is passed through the heated graphite atomizer form a source 38 via a pipe line 40, in the conventional manner.

The introduction device 14 includes a sliding member which, as illustrated in Figures 1 to 3, includes a piston and rod assembly 42 mounted in a pneumatic cylinder 44 for vertical reciprocating action. A punch-like element 46 is provided on the lower end of the piston rod for engaging the sample container of the micro-pipette tip 30 to urge it downwardly into the introduction aperture 36. The cylinder 44 has an upper port 48 connected to a gas line 50. Inert gas may be supplied from the inert gas source 38, through valve 52, line 54 and valve 56. Alternatively, or in addition, inert gas may be supplied from an external source 58. The downstroke of the piston and rod assembly is effected by applying gas under pressure to the top of the piston, as at 60, and the return stroke is effected by relieving the gas pressure on the top of the piston, back through the connection 48, line 50, valve 56 and outlets 62, while a spring 64 acts upwardly on the bottom of the piston.

In addition, the cylinder 44 is provided with a second port 66, which is connected to the inert gas line 50 via line 68 containing a valve 70. The piston and rod assembly 42 contains a longitudinally extending gas duct 72 having an exit opening 74 at the bottom thereof and an inlet opening 76 at the upper end. As best seen in Figure 2, the upper inlet opening 76 is in alignment with the port 66 when the piston and rod assembly is in its lower position and, at this time, valve 70 is opened to allow a flow of inert gas under pressure to pass down through the gas duct 72 and into the open upper end of the micro-pipette tip 30 to force the sample 32 out of the micropipette tip into the graphite tube 34 of the atomizer 12. It will be appreciated that this gas flow also serves as a seal between the top of the micro-pipette tip 30 and the bottom of the punch-like element 46. A control unit 78 serves to inter-relate and control the functions of the valve 56, valve 70 and turntable 16, as will be described more fully hereinafter.

Figure 4 shows an alternative introduction device. In this embodiment, a motor 80 vertically reciprocates a sliding member 82 in guide 84. The sliding member 82 is provided with a punch-like element 46[1] and a longitudinally extending gas duct 72[1] which function in the same manner as their corresponding parts previously described. A control unit 78[1] serves to interrelate and control the functions of the motor 80, valve 70[1] and the turntable 16.

In operation, sample containers 30 containing samples are placed in the sample holding members 22, and the control unit 78 actuates the drive for turntable 16 so that it rotates one step or until one of the sample

containers is under the introduction device and over the introduction aperture 36. Then, the control unit 78 actuates valve 56 to close the outlet 62 and open the flow therethrough so that the inert gas under pressure from the supply source flows through line 50 and into the top of the cylinder 44 to thereby urge the piston and rod assembly downwardly from its position as seen in Figure 1 to its position as seen in Figure 2. This movement causes the punch-like element 46 to push the micro-pipette tip 30, carried in the holding member 22, downwardly against the force of the spring 24 into the introduction aperture 36 of the graphite tube 34.

At the bottom of the stroke, as seen in Figure 2, the inlet opening 76 is aligned with the port 66 and the control unit actuates the valve 70 so that inert gas under pressure flows down through the gas duct 72 and into the open top of the micro-pipette tip 30 to thereby force the sample 32 out of the micro-pipette tip and into the graphite tube cell 34 of the atomizer 12. After discharging the sample, the control unit 78 closes the valve 70 and closes the valve 56 with respect to the supply source and opens valve 56 with respect to the outlet 62. This action relieves the pressure on the top of the piston 42 so that the spring 64 moves the piston and rod assembly back to its upper position. At the same time, the spring 24 returns the holding member 22 to its upper position, as seen in Figure 1. Thereafter, the control unit 78 actuates the drive for the turntable 16 so that it rotates one step to position the next adjacent sample container under the introduction device and over the introduction aperture. The same procedure is then repeated for the next sample analysis.

WHAT WE CLAIM IS:—

1. A method of atomic absorption spectrometry in which successive samples to be analysed are introduced through an aperture into a graphite tube of a graphite tube cell by means of sample containers which are open at both ends and are arranged in sequence on a sample holding device, each sample container in succession being moved to a position, from which the sample is introduced into the graphite tube, and then returned to the initial position in the sample holding device after which the next sample container is similarly treated.

2. A method according to claim 1 in which each container is moved into position above the insertion aperture of the graphite tube, is pressed into the insertion aperture against the force of a spring by means of an introduction device and is held in this position until transfer of the sample into the graphite tube has been completed.

3. A method according to claim 1 or claim 2, in which each sample container is of capillary size and the sample is transferred into the graphite tube by means of a gas flow through the container.

4. A method according to claim 3, in which the gas flow through each sample container and the inert gas flow passing through the graphite tube cell are derived from a common source.

5. A method according to claim 2 and claim 4, in which each sample container is moved by a device by means of an inert gas flow derived from the same source as that passing through the graphite tube cell.

6. Apparatus for carrying out a method according to any one of the preceding claims, comprising a sample holding device located above the graphite tube cell and capable of stepwise movement for bringing successive sample containers in the form of micro-pipette tips open at both ends into a sampling position in line with the insertion aperture of the graphite tube, an introduction device in the form of a slider which is movable up and down in a guide for inserting the sample container in the sampling position in the insertion aperture, a source of pressure gas for forcing out the sample from the container into the graphite tube in the lowered position of the slider and a control device for synchronizing the actuation of the introduction device, the movement of the sample holding device and release of gas from the pressure source.

7. Apparatus according to claim 6 having a common support for the sample holding device and the introduction device and to which the graphite tube cell is removably attached.

8. Apparatus according to claim 6 or claim 7 in which the sample holding device is formed as a turntable provided near its edge with holders for micro-pipette tips.

9. Apparatus according to claim 8, in which each holder is slidable vertically in a guide under spring control.

10. Apparatus according to any one of claims 6 to 9, in which in the lowermost position of the slider the micro-pipette tip is held in the insertion aperture of the graphite tube against the force of a spring.

11. Apparatus according to claim 10 in which the slider has an internal passage and makes a sealing connection with a micro-pipette tip in the lowered position.

12. Apparatus according to claim 11 in which in the lowered position of the slider an otherwise closed valve is open and gas pressure for expelling the sample is applied to the micro-pipette tip via the internal passage.

13. Apparatus according to claim 12, in which the slider and the valve are controlled to operate in synchronism.

14. Apparatus according to claims 12 and 13, in which the valve is connected to the same source of inert gas flow as that which supplies the graphite tube cell.

15. Apparatus according to claim 14, in which the valve is arranged near the lower end of the guide of the slider in a connecting line between the guide and a line for inert gas flow to the graphite tube cell.

16. Apparatus according to any one of the claims 6 to 15, and including an electric motor driven by the control device for producing the up and down travel of the slider.

17. Apparatus according to any one of claims 6 to 15 and including a pneumatic drive controlled by the control device for producing the up and down travel of the slider.

18. Apparatus according to claim 17, in which the pneumatic drive includes a pneumatic cylinder connected to the inert gas supply to the graphite tube cell.

19. Apparatus according to claim 15 and claim 18, in which the guide of the slider is defined by the pneumatic cylinder.

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1497012 COMPLETE SPECIFICATION

1 SHEET This drawing is a reproduction of the Original on a reduced scale

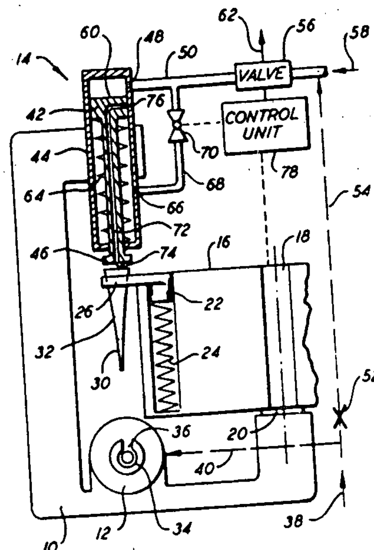

FIG. 1

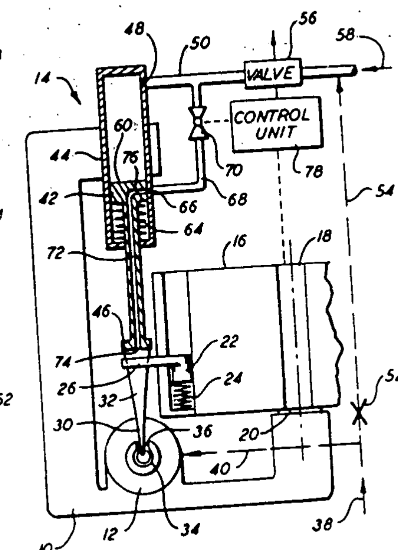

FIG. 2

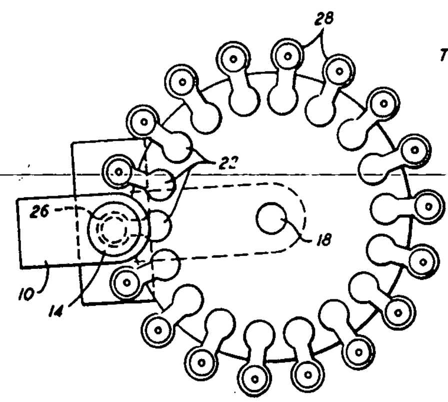

FIG. 3

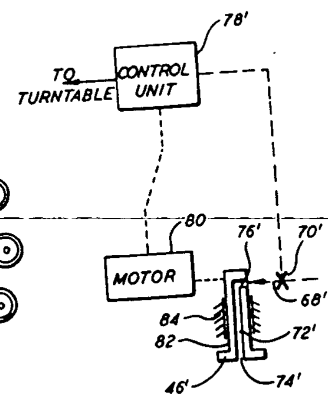

FIG. 4